

Porous TiO<sub>2</sub> nanowires derived from nanotubes:  
synthesis, characterization and their enhanced  
photocatalytic properties

*Zhen Jin, Fan-Li Meng, Yong Jia, Tao Luo, Jin-Yun Liu, Bai Sun, Jin Wang, Jin-Huai Liu and  
Xing-Jiu Huang\**

Research Center for Biomimetic Functional Materials and Sensing Devices, Institute of  
Intelligent Machines, Chinese Academy of Sciences, Hefei, 230031, China

\*Correspondence should be addressed to Xing-Jiu Huang

E-mail: xingjiuhuang@iim.ac.cn

Tel.: +86-551-5591142; fax: +86-551-5592420.

**Abstract:**

Anatase porous TiO<sub>2</sub> nanowires were synthesized *via* simple *in situ* hydrothermal treatment of the amorphous anodic TiO<sub>2</sub> nanotubes in urea aqueous solution at 70 °C. The morphology transformation process was also analyzed so that hydroxide induced dissolution-recrystallization mechanism was proposed. Due to the coarse surface and porous structure, the porous TiO<sub>2</sub> nanowires possess a large surface area of 267.56 m<sup>2</sup>g<sup>-1</sup>, which is almost 4 times higher than that of amorphous anodic TiO<sub>2</sub> nanotubes. The photocatalytic properties of the porous TiO<sub>2</sub> nanowires towards MB, phenol and Rhodamine 6G were investigated. The porous TiO<sub>2</sub> nanowires display better photocatalytic activity than that of TiO<sub>2</sub> nanotubes or Degussa P25. The enhanced photocatalytic activity is attributed to the porous structure and the large specific surface area. Such porous TiO<sub>2</sub> nanowires maybe considered as an ideal photocatalyst for the rapid photodegradation of organic pollutant in water. Furthermore, this facile, low-cost and environmentally friendly method is highly expected to innovate the design and fabrication of highly photoactive porous TiO<sub>2</sub> nanowires, which have potential applications in photocatalysis and solar energy conversion.

*Keywords:* TiO<sub>2</sub>; porous nanowires; structure transformation; dissolution-recrystallization; photocatalytic activity.

## 1. Introduction

Titanium dioxide ( $\text{TiO}_2$ ), as one of the most commonly used semiconductor materials, has attracted a lot of attention due to its unique photoinduced activity explored for applications in photocatalysis, environmental pollution control, and solar energy conversion. Due to these reactions usually taking place on the surface of  $\text{TiO}_2$ , the properties are strongly related to the surface area and local microstructures. Therefore, nanoscaled  $\text{TiO}_2$  with large surface area and specific morphology have attracted great attention. Up to today, many methods, such as anodization, template techniques, hydrothermal processes, and soft chemical processes have been used to synthesize  $\text{TiO}_2$  nanomaterials with high photocatalytic activity. Amongst these synthesis strategies, the electrochemical anodization process as a facile, cheap and straightforward method has been widely utilized to large-scaled preparation of  $\text{TiO}_2$  nanotubes with controllable size and morphology. However, smooth surface, relative low surface area and the amorphous structure of the obtained anodic  $\text{TiO}_2$  nanotubes result in low light utilization efficiency and photogenerated charges separation efficiency, thus leading to the poor photocatalytic activity. Many efforts have been made to enhance the photocatalytic activity of the anodic  $\text{TiO}_2$  nanotubes. For example, annealing of anodic  $\text{TiO}_2$  nanotubes in air contributes to converting the amorphous  $\text{TiO}_2$  into anatase, which can efficiently enhance the photocatalytic performance. Decorating the anodic  $\text{TiO}_2$  nanotubes with the other materials, such as noble metals and other semiconductors, can also improve the photocatalytic performance. However, those methods are expensive and high energy consumption. Recently, considerable efforts have been shifted to the architecture of 1D  $\text{TiO}_2$  hierarchical nanostructures derived from  $\text{TiO}_2$  nanotubes. By adjusting the phase and microstructure of the anodic  $\text{TiO}_2$  nanotubes, desired high photocatalytic activity can be achieved. For example, through a derivative anodic method, tube-in-tube  $\text{TiO}_2$  nanostructure possessing high surface area were synthesized, which showed

enhanced photocatalytic performance. Hierarchical TiO<sub>2</sub> nanotubes were obtained via chemical etching of the anodic TiO<sub>2</sub> nanotubes, exhibiting high photocatalytic activity due to their good crystallinity. Despite the great efforts contributed by many groups, seeking strategies for constructing anodic TiO<sub>2</sub> nanotubes with high surface area and anatase phase has still been an attractive ongoing task.

Herein, we demonstrate the synthesis of porous TiO<sub>2</sub> nanowires composed of anatase TiO<sub>2</sub> nanoparticles at low temperature *via* in situ hydrothermal treatment towards amorphous anodic TiO<sub>2</sub> nanotube arrays. Due to the coarse surface and porous structure, the porous TiO<sub>2</sub> nanowires possess a large surface area of 267.56 m<sup>2</sup>g<sup>-1</sup>, which is almost 4 times higher than that of amorphous anodic TiO<sub>2</sub> nanotubes. The anatase porous structure and large surface area of the porous TiO<sub>2</sub> nanowires lead to great enhancement of the photodegradation of organic pollutants. The photodegradation rate of the organic pollutant methylene blue (MB) under UV irradiation from the porous TiO<sub>2</sub> nanowires is 4.5 times faster than that from the amorphous TiO<sub>2</sub> nanotubes, and even higher than that from Degussa P25. In addition, the porous TiO<sub>2</sub> nanowires exhibit high photocatalytic activity in degrading phenol and Rhodamine 6G (R6G) as well. This facile, cost-effective and environmentally friendly method is anticipated to innovate the fabrication of highly photoactive porous TiO<sub>2</sub> nanowires, which have potential applications in environment and solar energy conversion.

## 2. Experimental

All reagents were commercially available from Sinopharm Chemical Reagent Co., Ltd (China) with analytical grade and were used without further purification. Degussa P25 TiO<sub>2</sub> (80% anatase and 20% rutile) was purchased from Guangzhou Huali Sen Trading Co., Ltd. The average particle size of P25 is 21 nm, and the specific surface area of which is 45.96 m<sup>2</sup>/g.

The synthesis of the porous TiO<sub>2</sub> nanowires was divided into two steps. Firstly, TiO<sub>2</sub> nanotubes were fabricated by anodizing the pure Ti sheet as described previously. In brief, the high-purity (99.999%) titanium plate was anodized in mixing electrolyte of ethylene glycol and ammonium fluoride (0.1 M) for 4 h. The anodizing voltage was 60 V and the temperature of the electrolyte was kept at 20 °C. Subsequently, the sample was rinsed with deionized water. Then, the as-fabricated TiO<sub>2</sub> nanotubes were put into a vessel which contained 0.1 M urea solution (100 ml). After heating at 70 °C for 10 h, white plates were collected from the solution. The as-prepared porous TiO<sub>2</sub> nanowires were washed with deionized water and dried in air.

The anatase TiO<sub>2</sub> nanotubes were synthesized by annealing the as-prepared anodic TiO<sub>2</sub> nanotubes at 500°C for 2 hours.

The morphologies of the samples were examined by field-emission scanning electron microscopy (FE-SEM; FEI Sirion-200) and high resolution transmission electron microscopy (HRTEM; JEM-2010). The crystal structure of the samples was determined by x-ray diffraction (XRD, Philips X'pert PRO) with Cu K<sub>α</sub> radiation.

The photocatalytic activities of the various samples were evaluated based upon the removal of stimulated organic pollutants, such as methylene blue (MB), phenol and R6G in the solution. In a typical photocatalytic experiment, 50 mL aqueous solution containing certain amount of stimulated organic pollutants and the as-synthesized product (30 mg) deprived from Ti foil, as catalyst, was maintained in suspension by a magnetic stirrer. A 150 W high pressure mercury lamp with a maximum emission at 365 nm was positioned at about 10 cm above the photo-reactor. Prior to irradiation, the suspension was ultrasonicated for 3 min and magnetically stirred for 1 h in dark to ensure adsorption-desorption equilibration. Then, UV light was turned on. During the given time intervals, 4 mL of solution has been taken from the suspension and

centrifuged at 10,000 rpm for 5 min to remove catalysts. The concentrations of MB, phenol and R6G were monitored by UV-vis spectroscopy (CARY-5E).

### 3. Results and Discussion

#### 3.1. Structure of the Porous TiO<sub>2</sub> nanowires.

Figure 1a and b show the top-view and cross-sectional SEM images of the anodic TiO<sub>2</sub> nanotubes. The open mouth and the closed end of the tubes with ca. 165 nm outer diameters can be clearly observed. Moreover, the inner diameters of the nanotubes at top side are larger than those at bottom side, indicating the taper hollow structure of the nanotubes. If the product is treated via urea, the open mouth can be disappeared, which is shown from the top-view SEM image in figure 1c. And urea treatment cause formation of rough surface, as shown in figure 1d. The cross-sectional images of treated products in figure 1e and f show disappearance of tube-like structure.

TEM was also employed to characterize the samples before and after urea treatment. Figure 2a shows a typical TEM image of the anodic TiO<sub>2</sub> nanotubes, demonstrating the diameter of 160 nm, which is in agreement with the SEM results. The corresponding selected area electron diffraction pattern (SAED) (the inset of figure 2a) indicates the amorphous structure of the anodic TiO<sub>2</sub> nanotubes. TEM images of urea-treated products are shown in figure 2b. Surprisingly, it is very clear that the tube-like structure is transformed to the rough porous nanowires after urea treatment. Furthermore, it can be observed that the obtained nanowires are composed of nanoparticles. The SAED pattern shown in inset of figure 2b presents series of concentric rings with different radii, indicating their polycrystalline nature of the porous TiO<sub>2</sub> nanowires. HRTEM image shown in figure 2c shows that the fringe spacing are 0.47 nm and 0.35 nm, respectively, which match well with those of the lattice space of (002) and (101) of anatase TiO<sub>2</sub>. Figure 2d shows the representative EDS spectra of porous nanowires, the molar

ratio of Ti:O is 1:1.93, which is very close to the stoichiometry of  $\text{TiO}_2$ . Figure 2e is the corresponding XRD pattern of the  $\text{TiO}_2$  nanotubes and porous  $\text{TiO}_2$  nanowires. As for  $\text{TiO}_2$  nanotubes, no diffraction peak was observed, which is in agreement with the SAED result. However, all of the diffraction peaks should be indexed to  $\text{TiO}_2$  anatase (JCPDS File 89-4203) after urea-treatment, and the amorphous  $\text{TiO}_2$  could be changed to crystalline  $\text{TiO}_2$ . More importantly, the tube-like structures are turned into anatase porous  $\text{TiO}_2$  nanowire. Previous reports indicated that the amorphous anodic  $\text{TiO}_2$  nanotubes always need to calcine at about 500 °C in the air so as to achieve anatase polycrystalline. In contrast, the amorphous anodic  $\text{TiO}_2$  nanotubes can be conveniently transformed to anatase porous nanowire at the temperature as low as 70 °C in present experiments.

### 3.2. Structure change mechanism

To study the morphological evolution from  $\text{TiO}_2$  nanotubes to porous  $\text{TiO}_2$  nanowires, time-dependent experiments were performed. Figure 3 shows the products prepared at different growth stages, i.e., the left, middle and right columns corresponding to the top side, lower part SEM images and TEM images, respectively. Initially, the  $\text{TiO}_2$  nanotubes as the precursor were added into urea solution under 70°C. Figure 3a presents the morphology of  $\text{TiO}_2$  nanotubes, as described before, in which the nanotubular structure and smooth surface wall can be observed clearly. Although the  $\text{TiO}_2$  nanotubes remain nanotubular structure after 2h, the open mouth becomes smaller both at the top side (the left in figure 3b) and lower part (the middle in figure 3b). As seen from the corresponding TEM image (the right in figure 3b), the smooth nanotubes turned to be rough and porous nanotubes, which are composed of nanoparticles. When prolonging the treated time to 4h, the open mouths of the nanotubes at the top side can still be observed, but the diameter of the open mouths decreases (the left in figure 3c); at the lower part, the former opened mouths were closed, indicating the formation of nanowire (the middle in

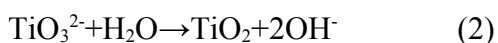
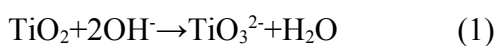
figure 3c). Interestingly, the corresponding TEM image (the right in figure 3c) shows the combination of the porous nanotube and porous nanowire. Accompany with the reaction time further prolonging to 6h, it can be found that at both the top side and lower part (the left and middle in figure 3d), the open mouths disappear, and the corresponding TEM image (the right in figure 3d) also illustrates the nanowire structure.

### 3.3 Growth mechanism

Based on the above experimental results and analysis, we propose that the morphology evolution of the porous  $\text{TiO}_2$  nanowires could be attributable to dissolution-recrystallization process, as shown in figure 4. It is well known that  $\text{TiO}_2$  is amphoteric oxide, besides acid solution, it also can slightly dissolve in alkaline solutions. In our case, the  $\text{TiO}_2$  nanotubes were immersed into urea solution (shown in figure 4a). When the solution was heated at  $70^\circ\text{C}$ , hydroxyl ions can be generated because of hydrolysis of the urea, resulting in the alkalization of the solution. In heated solutions, the surface atoms of  $\text{TiO}_2$  nanotubes would firstly act with hydroxyl ions to form  $\text{TiO}_3^{2-}$ , as described in equation 1. As the dissolution of  $\text{TiO}_2$  nanotube walls continues, the  $\text{OH}^-$  inside the nanotube is consumed faster than that outside of the nanotube, because the  $\text{OH}^-$  inside the nanotube is difficult to exchange with that outside the nanotubes by the confinement of the nanoscaled hole of the nanotube. When the concentration of  $\text{OH}^-$  inside the nanotube decreases to a certain value,  $\text{TiO}_3^{2-}$  presents a hydrolytic reaction to transform into  $\text{TiO}_2$ , as shown in equation 2. The recrystallized  $\text{TiO}_2$  spontaneously nucleates onto the residual nanotube frame, which can provide many high-energy sites for nanocrystallines (shown in figure 4b, 3b). As the etching proceeds, more and more  $\text{TiO}_2$  nuclei can be formed and grown up within the nanotubes. As the result of the etching of the  $\text{TiO}_2$  frames and the formation and growth of  $\text{TiO}_2$  nuclei nanocrystallines, the inner space of the nanotube was gradually occupied by  $\text{TiO}_2$  nanocrystallines, and the diameter of the nanotube gradually decreased. As



described before, the as-prepared TiO<sub>2</sub> nanotubes possess taper hollow structure, thus, the narrow part at the bottom would be fully occupied by TiO<sub>2</sub> nanocrystallines and firstly transformed to porous nanowires while the upper part remain nanotubular morphology (as shown in figure 4c, 3c). However, the reaction will not stop in that TiO<sub>2</sub> prefers to nuclei and growth on upper part after bottom part is fully occupied. With the increase of reaction time, the upper part of TiO<sub>2</sub> nanotubes would be full of TiO<sub>2</sub> nanocrystals, and the whole nanotube finally transformed into nanowires composed of TiO<sub>2</sub> nanocrystals (figure 4d, 3d).



### 3.4 N<sub>2</sub> adsorption–desorption analysis

The microstructure of the porous TiO<sub>2</sub> nanowires was further characterized with the N<sub>2</sub> adsorption/desorption isotherms. Figure 5a and b present the nitrogen adsorption–desorption isotherms and BJH pore size distribution curves of the TiO<sub>2</sub> nanotubes and porous TiO<sub>2</sub> nanowires. Both samples exhibited a type IV isotherm of a type H3 hysteresis loop (according to IUPAC classification), typical of mesoporous materials. The pore size distribution of the TiO<sub>2</sub> nanotubes shows a bi-modal size distribution, with the smaller sizes peaking at 20 nm and the larger sizes at 100 nm. The smaller mesopores can be related to the pores formed between stacked nanotubes, while larger mesopores reflect the hollow structure of the nanotubes. The pore size of the porous TiO<sub>2</sub> nanowires also exhibit two distributions, with the smaller sizes peaking at sub 2 nm and the larger sizes at 20 nm. The larger mesopores can also be related to the pores formed between stacked nanowires, and the smaller mesopores would be attributed to be the stack of nanoparticles within nanowires. The nanoholes within nanotubes are occupied by nanoparticles due to the urea-treatment. As a result, the pore sizes peak of 100 nm within porous TiO<sub>2</sub> nanowires vanishes while the peak of 10 nm appeared, which further confirmed the SEM

and TEM results. The BET specific surface area and pore volume of the porous TiO<sub>2</sub> nanowires is determined to be 267.56 m<sup>2</sup>g<sup>-1</sup> and 0.31 cm<sup>3</sup>g<sup>-1</sup>, respectively, which are significantly higher than the values of porous TiO<sub>2</sub> nanowires (70.28 m<sup>2</sup>g<sup>-1</sup> and 0.12 cm<sup>3</sup>g<sup>-1</sup>). Hence, the porous TiO<sub>2</sub> nanowires could be considered as a promising photocatalytic candidate for water treatment thanks to high BET surface area, high value of pore volume and ideal pore size distribution.

### 3.5 Optical properties

The optical properties of the porous TiO<sub>2</sub> nanowires and TiO<sub>2</sub> nanotubes were investigated by UV-vis diffuse reflectance spectra (Figure 6). It can be seen that, there is a small peak at 474nm within the spectrum of the TiO<sub>2</sub> nanotubes, while no peak can be observed to the porous TiO<sub>2</sub> nanowires, indicating the color change from brown to white. Furthermore, compared to TiO<sub>2</sub> nanotubes, the porous TiO<sub>2</sub> nanowires showed the higher UV light absorption. Obviously, the UV-vis absorption would be affected considerably by the morphological changes, and the rough surface and porous structure of the porous TiO<sub>2</sub> nanowires can allow multiple reflections of UV light, which enhances light-harvesting and thus increases the quantity of photogenerated electrons and holes available to participate in the photocatalytic decomposition process.

### 3.6 Photocatalytic activity

As far as TiO<sub>2</sub> photocatalyst is concerned, the anatase phase and surface area are the most important criteria.. High photocatalytic efficiency of the porous TiO<sub>2</sub> nanowires could be expected due to the anatase phase and high surface area within the porous TiO<sub>2</sub> nanowires. In order to demonstrate the functionality of the as-fabricated porous TiO<sub>2</sub> nanowires, their photocatalytic activity was evaluated based on the removal of methylene blue (MB) dye in the aqueous solution. For comparison, the photocatalytic activity of the amorphous TiO<sub>2</sub> nanotubes, anatase TiO<sub>2</sub> nanotubes and P25 particles are also investigated. Figure 7a displays the variation of the photocatalytic activity of different samples determined at the maximal absorption

wavelength of MB (664nm) with the time of irradiation. As expected, the porous TiO<sub>2</sub> nanowires exhibit superior photocatalytic performance than other photocatalysts. MB is almost completely photodegraded by the porous TiO<sub>2</sub> nanowires within 80 minutes, while 40%, 75% and 90% of MB are removed by amorphous TiO<sub>2</sub> nanotubes, anatase TiO<sub>2</sub> nanotubes and P25, respectively. As shown in figure 7b, the MB photodegradation kinetics of various photocatalysts were also investigated. After the natural logarithm of residual phenol concentration vs UV irradiation time, the linear relationship of  $\ln(C_0/C)$  vs time shows that the photoelectrocatalytic degradation of MB follows pseudofirst-order kinetics:  $\ln(C_0/C) = kt$ , where  $C_0/C$  is the normalized MB concentration,  $t$  is the reaction time, and  $k$  is the apparent reaction rate in  $\text{min}^{-1}$ . The apparent photodegradation rate constant by the porous TiO<sub>2</sub> nanowires is  $0.0426 \text{ min}^{-1}$ , which is 4.35 times more than that of amorphous TiO<sub>2</sub> nanotubes ( $0.0098 \text{ min}^{-1}$ ), 2.18 times than that of anatase TiO<sub>2</sub> nanotubes ( $0.0195 \text{ min}^{-1}$ ) and 1.26 times than that of P25 ( $0.0337 \text{ min}^{-1}$ ). Besides MB, phenol and R6G with the concentration of  $15 \text{ mg L}^{-1}$  were also employed to evaluate the photocatalytic activity of the porous TiO<sub>2</sub> nanowires. From figure 8a and b, it is clearly that, towards phenol and R6G, the porous TiO<sub>2</sub> nanowires also exhibit higher photocatalytic performance than other samples. Both of phenol and R6G can be completely photodegraded by the porous TiO<sub>2</sub> nanowires within 30 minutes. Such dramatic enhancement of catalytic activity can be attributed to the synergistic effects of morphology and structure transformation. Firstly, the anatase structure of porous TiO<sub>2</sub> nanowires would facilitate electron transfer from bulk to surface, and thus inhibit their recombination with photoinduced holes, leading to higher quantum efficiency. Meanwhile, the porous TiO<sub>2</sub> nanowires possess much higher BET surface area than TiO<sub>2</sub> nanotubes, and the increase of the surface area can provide more active catalytic sites. Furthermore, the porous structured of TiO<sub>2</sub> nanowires with smaller textural mesopores and larger pore volume would provide reactant substances of different size transport circumstances as

compared to those in open medium, and expedite mass transportation. In addition, the compact stacked nanoparticles within porous TiO<sub>2</sub> nanowires can allow multiple reflections of UV light, which enhances light-harvesting and thus increases the quantity of photogenerated electrons and holes available to participate in the photocatalytic degradation of organic pollutions. These factors are beneficial to form more surface hydroxyl radicals to enhance the photocatalytic degradation of phenol. Additionally, based on the well-known fact that anatase phase TiO<sub>2</sub> possesses higher photocatalytic activity than amorphous TiO<sub>2</sub>, the anatase phase characteristics of the present porous TiO<sub>2</sub> nanowires after urea-treatment exhibits superior photocatalytic behaviors. Therefore, it can be concluded that porous TiO<sub>2</sub> nanowires can be acted as excellent photocatalysts.

The renewable photocatalytic activity has to be investigated in that the reuse performance is also a key role for the applications of photocatalytic materials. The result is presented in the same manner as shown in figure 9, from which we can see that the photocatalytic activity of the porous TiO<sub>2</sub> nanowires is very stable. Even if after 5 cycles under UV irradiation, more than 90% of MB was degraded within 80 min, indicating that the porous TiO<sub>2</sub> nanowires is stable and effective for the removal of organic pollutants in water. Obviously, the porous TiO<sub>2</sub> nanowire prepared in our experiments is a promising photocatalyst due to its excellent activity and good recycle performance.

#### **4. Conclusions**

In conclusion, anatase porous TiO<sub>2</sub> nanowires have been produced spontaneously from anodized amorphous TiO<sub>2</sub> nanotubes in urea solution at a temperature as low as 70 °C. The phase and morphology transformation process of the TiO<sub>2</sub> nanotubes are characterized and a mechanism of hydroxide induced dissolution and recrystallization is proposed. Due to the hydrolysis of urea, the amorphous TiO<sub>2</sub> nanotube walls can be gradually etched by hydroxyl ions

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and dissolved. When the concentration of  $\text{OH}^-$  inside the nanotubes decreases to a threshold value, the dissolved  $\text{TiO}_2$  can recrystalline from solution, and nucleate onto the residual nanotube frame and grow up within the nanotubes. During the dissolve-recrystalline process, more and more  $\text{TiO}_2$  nuclei has been formed and grown up within the nanotubes, finally fulfilled the inner space of nanotubes for yielding anatase porous  $\text{TiO}_2$  nanowires. The surface area of porous  $\text{TiO}_2$  nanowires reaches  $267.56 \text{ m}^2\text{g}^{-1}$ , which is almost 4 times higher than that of  $\text{TiO}_2$  nanotubes. The photodegradation rate of the organic pollutant mehtylene blue (MB) under UV irradiation by the porous  $\text{TiO}_2$  nanowires is 4.35 times higher than that of the  $\text{TiO}_2$  nanotubes, and much higher than that of Degussa P25. Besides degrading MB, the porous  $\text{TiO}_2$  nanowires also exhibit high photocatalytic activity in degrading phenol and R6G. The enhanced photocatalytic activity achieved from the porous  $\text{TiO}_2$  nanowires is ascribed to the porous structure and large surface area. The results demonstrate a facile and practical route for designing and architecting highly photoactive 1D  $\text{TiO}_2$ -based porous functional materials, which have potential use in photocatalysis and solar energy conversion.

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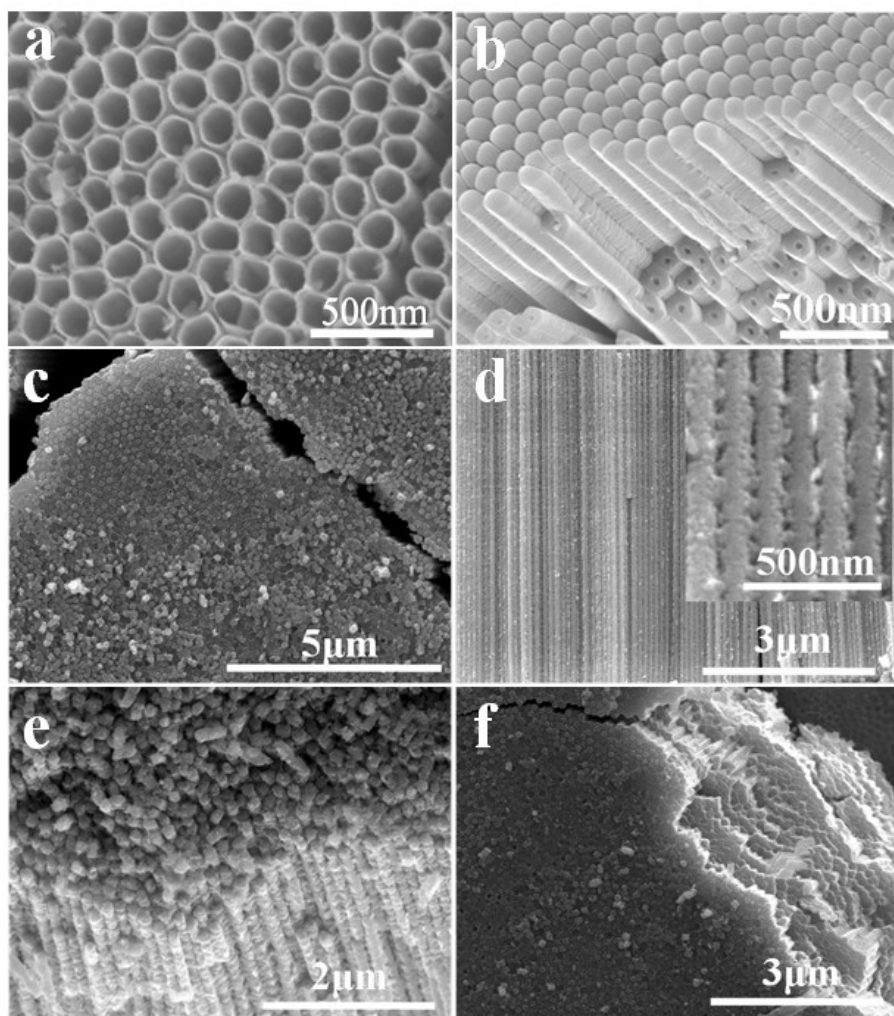
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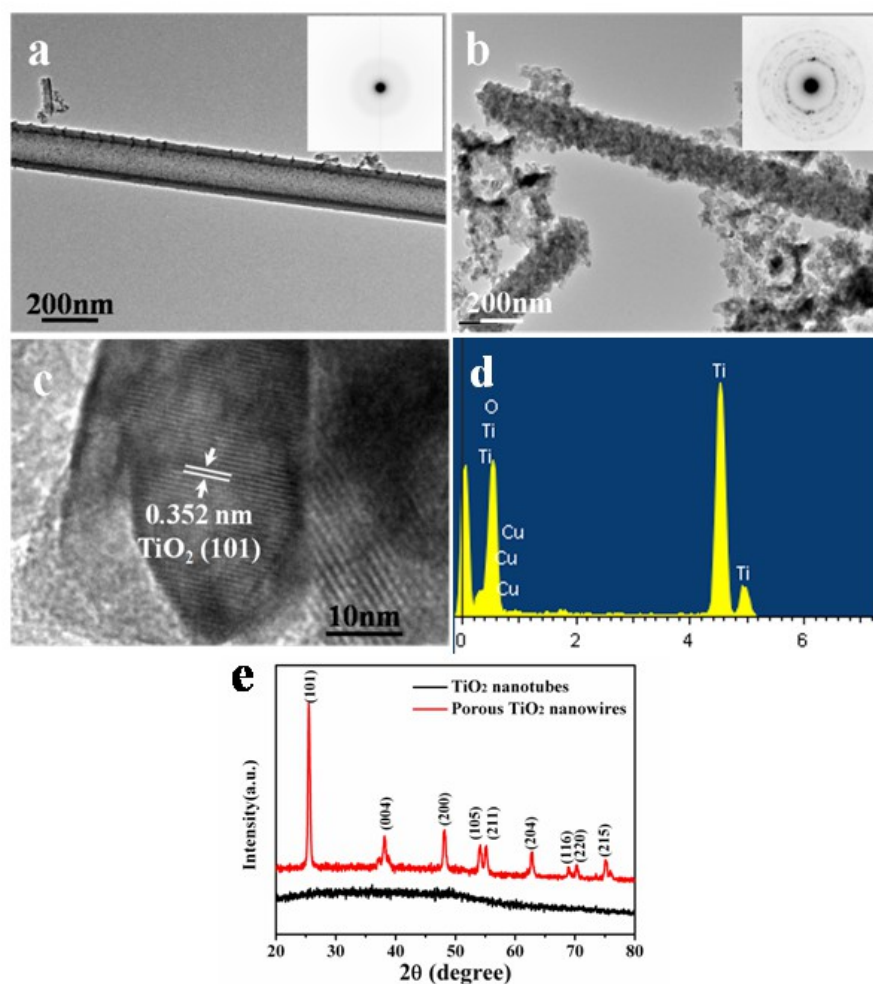
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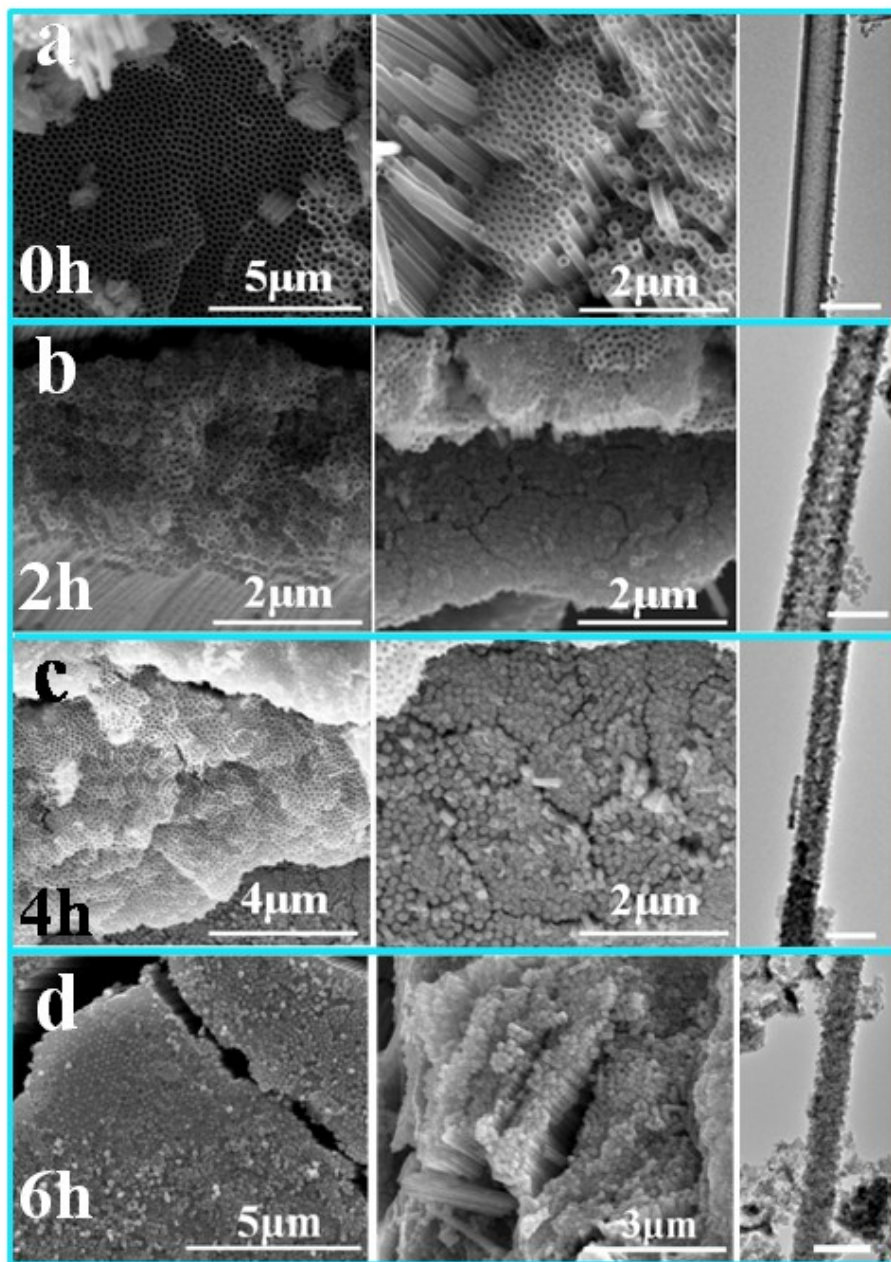
**Figures:**



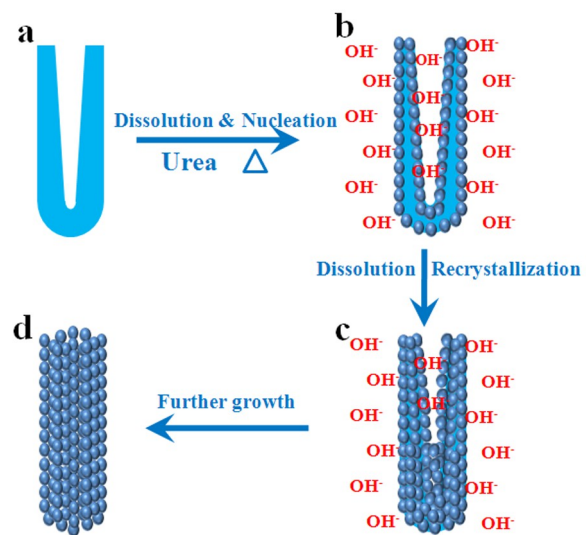
**Figure 1.** SEM images of  $\text{TiO}_2$  nanotubes and porous  $\text{TiO}_2$  nanowires: (a, b) top-view of the anodic  $\text{TiO}_2$  nanotubes, (b) cross-section and surface view of the bottom side of the anodic  $\text{TiO}_2$  nanotubes, (c) top-view of the porous  $\text{TiO}_2$  nanowires, (d) cross-section images of the porous  $\text{TiO}_2$  nanowires, the inset is the enlarged image, (e) high and (f) low magnifications cross-section and surface view of the porous  $\text{TiO}_2$  nanowires.



**Figure 2.** (a) TEM image of a single  $\text{TiO}_2$  nanotube (inset is the corresponding SEAD), (b) TEM image of the porous  $\text{TiO}_2$  nanowires (inset is the corresponding SEAD), (c) HRTEM image of the porous  $\text{TiO}_2$  nanowires, (d) EDS of the porous  $\text{TiO}_2$  nanowires, (e) XRD pattern of the  $\text{TiO}_2$  nanotubes and porous nanowires.

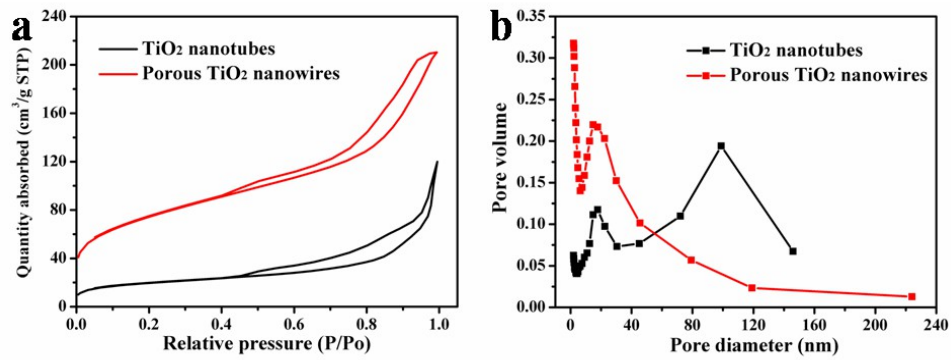


**Figure 3.** Morphology transformation from the  $\text{TiO}_2$  nanotubes at different reaction times: (a) 0 h; (b) 2 h; (c) 4 h; (d) 6 h. The left and middle columns show the SEM images of the top and lower part, while the third column shows the corresponding TEM images of  $\text{TiO}_2$  nanostructures.

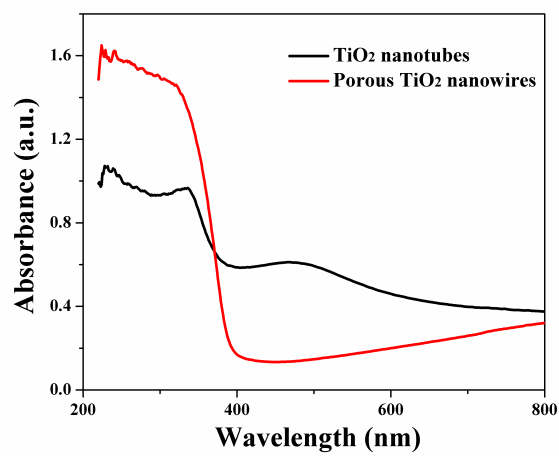


**Figure 4.** Schematic illustration of the morphological transformation from the TiO<sub>2</sub> nanotubes to the porous nanowires.



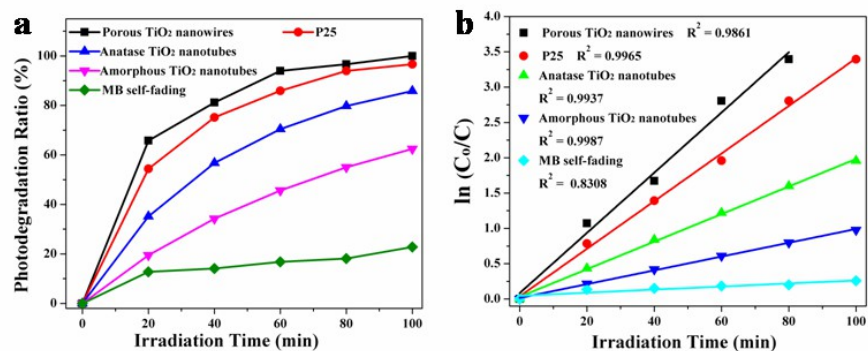


**Figure 5.** (a) N<sub>2</sub> adsorption-desorption isotherm of the TiO<sub>2</sub> nanotubes and porous TiO<sub>2</sub> nanowires, and (b) the corresponding pore size distribution.

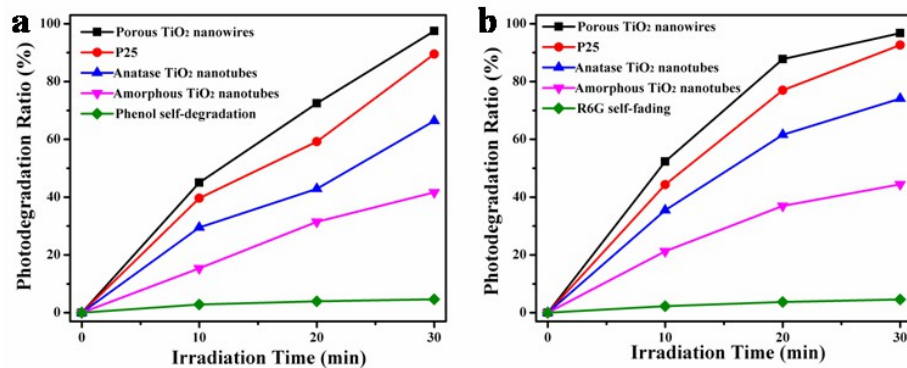


**Figure 6.** UV-vis absorption spectrum of the TiO<sub>2</sub> nanotubes and porous TiO<sub>2</sub> nanowires.

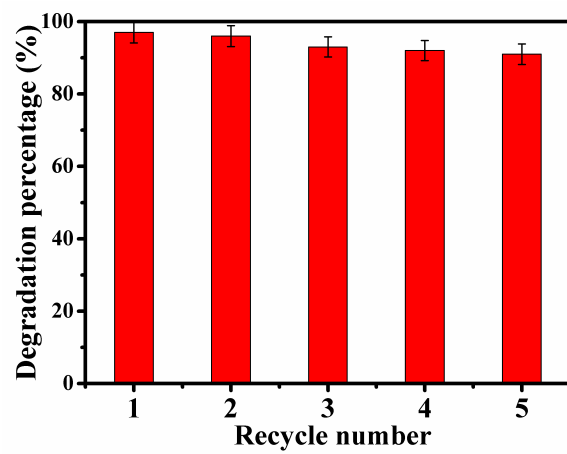




**Figure 7.** (a) The variation of photocatalytic degradation ratio of MB over the porous TiO<sub>2</sub> nanowires, amorphous TiO<sub>2</sub> nanotubes, anatase TiO<sub>2</sub> nanotubes, P25 and self-fading, (b) the pseudo first-order kinetic rate plots for the photodegradation of MB.



**Figure 8.** The variation of photocatalytic degradation of phenol (a) and R6G (b) over the porous TiO<sub>2</sub> nanowires, anatase TiO<sub>2</sub> nanotubes amorphous TiO<sub>2</sub> nanotubes, P25 and self degradation with time of irradiation.



**Figure 9.** Cyclic degradation of MB by porous TiO<sub>2</sub> nanowires.